

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
24 October 2002 (24.10.2002)

PCT

(10) International Publication Number
WO 02/084278 A1

BEST AVAILABLE COPY

(51) International Patent Classification⁷: **G01N 31/22**,
21/78, 33/18

(21) International Application Number: PCT/GB02/01515

(22) International Filing Date: 9 April 2002 (09.04.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0108926.7 10 April 2001 (10.04.2001) GB

(71) Applicant (*for all designated States except US*):
RECKITT BENCKISER (UK) LIMITED [GB/GB];
103-105 Bath Road, Slough, Berkshire SL1 3UH (GB).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **MCKECHNIE, Malcolm, Tom** [GB/GB]; Reckitt Benckiser Corporate Services Limited, Dansom Lane, Hull HU8 7DS (GB). **CORNELIUS, Gay, Joyce** [GB/GB]; Reckitt Benckiser Corporate Services Limited, Dansom Lane, Hull HU8 7DS (GB). **COKE, Mark** [GB/GB]; Reckitt Benckiser Corporate Services Limited, Dansom Lane, Hull HU8 7DS (GB).

(74) Agents: **BROWN, Andrew, Stephen et al.**; Reckitt Benckiser plc, Group Patents Department, Dansom Lane, Hull HU8 7DS (GB).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:

— *of inventorship (Rule 4.17(iv)) for US only*

Published:

— *with international search report*
— *with amended claims*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: INDICATOR FOR CALCIUM AND MAGNESIUM

(57) Abstract: The application relates to a composition for detecting Calcium or Magnesium ions (i.e. water hardness) comprising a metal indicator dye selected from the group of Alizarin Red, Eriochrome Black, Calmagite, or Murexide, the indicator dye being impregnated in a sheet of a fibrous material.

WO 02/084278 A1



INDICATOR FOR CALCIUM AND MAGNESIUM

The invention relates to a product, preferably a fibre product, having bound to it an anionic metal ion indicator dye, and use of such products in the detection of metal ions, in particular calcium ions, in a liquid.

The ability to test for the presence of metal ions in a liquid is a requirement in many fields, such as water treatment (for example, for detecting heavy metals), laundry (testing for water hardness), health (metal ion concentrations are measured in blood plasma, urine and other bodily fluids). Current tests utilise dyes sensitive to the presence of metal ions such that their colour changes. These may be added directly to a liquid and the colour change detected for a qualitative measurement or the colour change may be titrated, in certain cases, to give a reasonably accurate quantitative measure of the metal ion concentration.

20

In certain situations it is not desirable to dye the liquid. Alternatively, therefore, dye is impregnated onto strips for dipping into a liquid. However, such strips can not be immersed and left in the liquid since, commonly, metal ion indicator dyes are aqueously soluble and will leach into the liquid.

25

We have identified a new, quick, simple and effective means for immobilising such dyes.

30

We present as a feature of the invention a product having bound to it an anionic metal ion indicator dye.

2 -

Any number of methods of binding the anionic metal ion indicator dye to the product would be contemplated, including ionic binding.

- 5 We present as a preferred feature of the invention a product having a cationic compound to which is ionically bound an anionic metal ion indicator dye.

Preferably the cationic compound is irreversible bound to the product. By "irreversible bound" we mean that less than 20% w/w, 15% w/w, 10% w/w, 5 % w/w, preferably less than 1 % w/w of the cationic compound is released from the cloth when immersed in an aqueous liquid for 60 minutes, where the temperature is less than 80° C, and
15 the pH is less than <10.5.

The product may be any suitable solid for immersion into a liquid. Suitable solids may be made from a polymer. In a preferred alternative the product is a fibre product, either of a synthetic fibre or a natural fibre.
20

The fibre product is ideally formed in some way preferably into a sheet, for example a woven, knitted or non-woven sheet. Alternatively it may be twisted into a yarn and, optionally, further formed into a thick yarn, or braid. Alternatively it may be in the form of fibres which may, for example, be tied together. The fibres may be retained in a water-permeable transparent or translucent bag. Most preferably the fibre is a fabric of relatively open form, for example a non-woven fabric or a woven fabric of scrim form.
25
30

3 -

Where the product is made from a polymer then this may take the form of a sheet, sponge or particulate. It will be appreciated that many polymers may be formed into a fibre. Suitable polymers are those which are positively
5 charged, cationic, and may include polyvinyl pyrrolidone and silicas, such as Macrosorb (Ineos Silicas).

Products to which are ionically bound a calcium ion indicator dye are particularly preferred. Calcium ion
10 indicators which can be bound are selected from; metalphthalein, 3,4-dihydroxy-9,10-diazo-2-anthracene sulfonic acid (Alizarin Red S), ammonium purpurate, 1-(1-hydroxy-2-naphthylazo)-5-nitro-2-naphthol-4-sulfonic acid (Eriochrome Black T) and 1-(1-hydroxy-4-methyl-2-
15 phenylazo)-2-naphthol-4-sulfonic acid (Calmagite).

A further feature of the invention is a method of detecting the presence of at least one type of metal ion within a liquid which comprises

20

1) immersing or immersing and removing (preferably just immersing) a product as described herein, and

2) observing the product for any change in colour.

25

Preferably the liquid is water and in particular it is a wash liquor. Alternatively the water may be; effluent, a bodily liquid or any other liquid in which the presence of a metal ion or its concentration may need to be
30 measured.

It will be appreciated that a colour change may occur when the anionic metal ion indicator dye is bound to the

4-

product - this is described in "Dyeing & Chemical Technology of Textile Fibres" Trotman E.R. 1964, Griffin Publishers. The possible colour change seen when a metal ion indicator dye is bound to the product may be
5 different or unexpected, as may the colour change when the product is exposed to the metal ion, compared with the colour change found in solution with the same metal ion indicator dye and metal ion. This in part has to do with the association of the metal ion indicator dye to
10 the product. However, we have found that despite the possibility of such differences a reliable and effective colour change can still successfully occur when the dye is bound to the product.

15 Preferably the product is able to move freely within the liquid. It could also be in the form of a filter or like body, retained in a fixed orientation, or mounted onto a frame.

20 In a preferred arrangement the product is are also able to bind metal ions, especially calcium ions so as to soften the water, by also having bound to the cationic compound on the product, not occupied with metal ion indicator dye, metal ion sequestrants. Most preferably
25 the sequestrants are also able to bind further ions, for example magnesium, copper and iron. Preferably any calcium ion sequestrant used is also able to bind such further ions. Alternatively, the product may have two, or more, types of metal ion sequestrant, able to bind
30 different metal ions. In such an arrangement it is preferred that the anionic metal ion indicator dye binds metal ions in preference to any anionic metal ion sequestrant present on the product.

5 -

The product may be prepared in any of a number of ways. The cationic compound may be grafted onto the product, for example, cationic compound may be bound to the
5 product by a number of well-known techniques, such as radiation grafting or chemical grafting. Radiation grafting is described in WO 94/12545. Chemical grafting is described in GB 2086954A.

10 Alternatively, for certain cationic compounds polymeric fibres may be fabricated (for example melt spun) already bearing the cationic compound, as described in EP 486934A. In yet other embodiments the polymeric fibres not bearing the cationic compound may be coated with
15 material which has the cationic compound. The polymeric fibres may, in effect, be regarded as carrying the cationic compound by mechanical adhesion. Alternatively cationic compound may be attached by cross-linking, as described in EP 992283A.

20

The anionic metal indicator dye may be bound to the product by impregnating into the products the anionic metal indicator dye, for example by aqueous solution or super critical liquid CO₂.

25

A suitable technique is described in EP 0210034 for the generation of fibre cloths having bound a cationic compound.

30 Suitable cloths bearing cationic groups may be purchased easily and anionic metal ion indicator dye added simply by immersing the cloth into a solution of the anionic metal ion indicator dye and rinsing excess dye off. For

6 -

example "Colour Catcher" ACDO Service Bureau, Bolton B21 8PP, England, www.acdo.co.uk, and "Woolite Colour Catcher" Reckitt Benckiser, Hull, UK, HU8 7DS, www.reckittbenckiser.com.

5

A further feature of the invention is a process for the preparation of a product, as defined herein, which comprises, immersing a product containing cationic groups into a solution of an anionic metal indicator dye and,
10 optionally, drying the product.

Due to the ionic nature of the binding of the anionic metal indicator dye to the cationic groups we have found that preferably the dye is bound to the cloth at pH
15 conditions of greater than 7, preferably greater than 8, ideally greater than 9.

The concentration of metal ions may be measured by comparing the colour change to a standardised calibration
20 colour change chart.

The metal ion indicator dye may be bound to the product in differing concentrations to provide the possibility of measuring the concentration of metal ions in the liquid
25 directly.

Typical concentrations of metal ion indicator dye which are used when immersing the product to bind the metal ion indicator dye are from 0.1 % w/w, preferably 0.03 % w/w,
30 to 0.0001 %w/w.

The metal ion indicator dye may be bound to the product in simple patterns such as circles or squares or may be

7-

deposited in a way so as to create pictures, numbers, letters or words.

Experimental

5

Example 1

Cloths ("Colour Catcher" ACDO Service Bureau, Bolton B21 8PP, England) were immersed in a 0.01 % Alizarin Red S solution for 10 minutes, rinsed in 300 ml of deionised water and used wet. A sample of the cloth was immersed in

- i) deionised water one at pH 7 and another at pH 10
- 15 ii) hard tap water (120 ppm/ml⁻¹?) one at pH 7 and another at pH 10

for 5 minutes. The sample in the deionised water remained purple and the two samples in hard tap water both turned a pink colour.

20

Example 2

Cloths ("Colour Catcher" ACDO Service Bureau, Bolton B21 8PP, England) were immersed in a 1.4 % Murexide solution for 10 minutes, rinsed in 300 ml of deionised water and used wet and dry. A sample of the cloth was immersed for 5 minutes with gentle agitation in

- 30 i) deionised water one at pH 7 and another at pH 10
- ii) hard tap water (120 ppm ml⁻¹) one at pH 7 and another at pH 10

8 -

for 5 minutes. The cloths in deionised water remained a straw colour whilst cloths in the hard tap water turned pink.

5

Examples 1 and 2 show a colour response with Ca^{2+} irrespective of pH.

Example 3

10

Cloths ("Colour Catcher") were immersed in 0.1 g Alizarin Red S in 300 ml deionised water, rinsed in 300 ml of deionised water, and dried. The cloth was a red/brown colour.

15

Examples 4 & 5

In a similar manner as Example 4, two additional cloths were prepared using Eriochrome Black T, producing a dark blue cloth, and Calmagite, producing a purple/red cloth.

20

Cloths from Examples 3, 4 and 5 were each tested in an electric automatic laundry machine at 60° C with an "Ariel Essential" tablet on an Easy Care Programme using hard tap water.

25

Example 3 the cloth after the wash was violet/purple.

Example 4 the cloth after the wash was light purple.

Example 5 the cloth after the wash was violet.

30

All, therefore, showed a colour change response, even in the presence of laundry detergent, to Ca^{2+} and at an elevated temperature.

Example 6

0.033g of Eriochrome Black T was dissolved in 1l of
5 deionised water. One Woolite Colour Catcher
(ReckittBenckiser Hull UK) cloth, dimensions 11.5cm x
21.5cm, was added to this solution and stirred for 20
minutes. The cloth was removed from the solution and
allowed to dry. The cloth treated in the manner above was
10 blue in colour. The cloth remained blue after being
immersed in deionised water, but turned purple in water
containing calcium. The colour did not bleed
significantly from the cloth upon immersion. The purple
colour is also evident in the cloth following a washing
15 machine cycle, carried out in hard water, at 60°C in the
presence of a heavy duty laundry detergent, which
contains a bleaching compound. Furthermore there is no
significant fading of this colour as a consequence of the
wash.

20

When a cloth is soaked in Eriochrome Black T at pH 10 (pH
adjusted with NaOH) then greater dye pick-up is seen than
without a pH adjustment of the solution. The cloth still
becomes blue upon immersion in the dye and changes to
25 purple in hard water as before.

Claims

1. A product having bound to it an anionic metal indicator dye.
5
2. A product as claimed in claim 1 wherein the anionic metal indicator dye is bound to a polymer.
3. A product as claimed in claim 1 wherein the anionic metal indicator dye is bound to a fibre, either
10 synthetic or natural.
4. A product as claimed in claim 1 having a cationic compound to which is ionically bound the anionic
15 metal ion indicator dye.
5. A product as claimed in claim 2 wherein the cationic compound is irreversible bound.
- 20 6. A product as claimed in claims 1 or 2 wherein the anionic metal ion indicator dye is sensitive to the presence of calcium ions.
7. A product, as claimed in claim 3 wherein the fibre is
25 formed into a woven, knitted or non-woven sheet.
8. A method of detecting the presence of at least one type of metal ion within a liquid which comprises
 - 1) immersing or inserting and removing (preferably
30 immersing) a product having bound to it an anionic metal ion indicator dye, and
 - 2) observing the product for any change in colour.

11 -

9. A method as claimed in claim 8 wherein the anionic metal indicator dye is bound to a polymer.
10. A method as claimed in claim 8 wherein the anionic metal indicator dye is bound to a fibre, either synthetic or natural.
11. A method as claimed in any claim from 8 to 10 wherein the anionic metal ion indicator dye is sensitive to the presence of calcium ions.
12. A method as claimed in claim 11 for measuring water hardness by performing the additional step of comparing the colour change to a calibrated colour chart to determine the hardness of the water.
13. A process for the preparation of a product, as defined in claim 4 or claim 5, which comprises, immersing a product containing cationic groups into a solution of an anionic metal indicator dye.
14. A process as claimed in claim 13 wherein the product is dried.
15. A process as claimed in claim 13 or 14, wherein the pH of the solution is adjusted to be greater than 7, preferably greater than 8, ideally greater than 9.
16. A process as claimed in any claim from 13 to 15 wherein the concentration of metal anionic ion indicator dye solution is from 0.1 % w/w, preferably 0.03 % w/w, to 0.0001 %w/w.

AMENDED CLAIMS

[received by the International Bureau on 09 August 2002 (09.08.02);
original claims 1, 9, 10, and 11 cancelled;
remaining claims amended and renumbered as claims 1-12 (2 pages)]

1. A product having a cationic compound to which is
ionically bound an anionic metal ion indicator dye.
5
2. A product as claimed in claim 1 wherein the anionic
metal indicator dye is ionically bound to a polymer.
3. A product as claimed in claim 1 wherein the anionic
10 metal indicator dye is ionically bound to a fibre,
either synthetic or natural.
4. A product as claimed in claim 1 wherein the
cationic compound is irreversible bound to the
15 product.
5. A product as claimed in any preceding claim wherein
the anionic metal ion indicator dye is sensitive to
the presence of calcium ions.
20
6. A product, as claimed in claim 3 wherein the fibre is
formed into a woven, knitted or non-woven sheet.
7. A method of detecting the presence of at least one
25 type of metal ion within a liquid which comprises
 - 1) immersing or inserting and removing (preferably
immersing) a product as defined in any claim
from 1 to 6, and
 - 2) observing the product for any change in colour.
- 30
8. A method as claimed in claim 7 for measuring water
hardness by performing the additional step of

comparing the colour change to a calibrated colour chart to determine the hardness of the water.

9. A process for the preparation of a product, as
5 defined in any claim from 1 to 6, which comprises,
immersing a product containing cationic groups into a
solution of an anionic metal indicator dye.
10. A process as claimed in claim 9 wherein the product
10 is dried.
11. A process as claimed in claim 9 or 10, wherein the pH
of the solution is adjusted to be greater than 7,
preferably greater than 8, ideally greater than 9.
- 15 12. A process as claimed in any claim from 9 to 11
wherein the concentration of metal anionic ion
indicator dye solution is from 0.1 % w/w, preferably
0.03 % w/w, to 0.0001 %w/w.

20

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 02/01515

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 G01N31/22 G01N21/78 G01N33/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 320 969 A (BAUER ROBERT ET AL) 14 June 1994 (1994-06-14) abstract column 12, line 54 -column 13, line 29 column 16, line 20 -column 17, line 3 ----	1-16
X	US 5 302 531 A (BAUER ROBERT) 12 April 1994 (1994-04-12) abstract column 8 -column 9 table 1 example 3 ----- -/-	1-16



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

Z document member of the same patent family

Date of the actual completion of the international search

2 July 2002

Date of mailing of the international search report

18/07/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Michalitsch, R

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 02/01515

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>DATABASE WPI Section Ch, Week 199018 Derwent Publications Ltd., London, GB; Class D15, AN 1990-134987 XP002204225 & JP 02 082160 A (MIURA KOGYO KK), 22 March 1990 (1990-03-22) abstract</p> <p>----</p>	1-16
Y	<p>DATABASE WPI Section Ch, Week 197706 Derwent Publications Ltd., London, GB; Class D15, AN 1977-10281Y XP002204226 & JP 51 150392 A (TOYO ROSHI KK), 22 December 1976 (1976-12-22) abstract</p> <p>-----</p>	1-16

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB 02/01515

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 2, 4, 5, 9, 13-16
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 2,4,5,9,13-16

claims searched in part: 1,3,6,7,8,10-12

Independent Claim 1 is directed towards a composition comprising an anionic metal indicator dye and a product bound to it. Independent claim 8 claims a method for detecting the presence of a metal ion using such a product. Independent claim 13, on the other hand, claims the preparation of the product.

-Claim 1 lacks clarity within the meaning of Article 6 PCT for the following reasons.

a) The indicator dye is according to claim 1 bound to a product, which is not specified, thereby rendering the entire claim unclear and extremely broad.

b) Furthermore, the anionic metal indicator dye in claim 1 can be interpreted in the following ways:

- as an indicator dye for "anionic metals" or
- a metal-indicator dye complex, which is present in its anionic form or
- an anionic indicator dye for detecting metals

However, in all cases, claim 1 would contradict the description, where the dye is selected from the group alizarin red, eriochrome black, calmagite, and murexide. These dyes, however, have no anionic nature per se.

Thus, it is not clear what exactly is claimed by claim 1.

The lack of clarity is compounded in the dependent claims.

-Claim 2 claims that the indicator dye of claim 1 is bound to a polymer. It is unclear if the polymer is the product of claim 1 or not.

-The same problem arises from claim 3, where the indicator dye is bound to a fibre.

-Claim 4 claims a cationic compound, which is bound to the indicator dye, although presumably a cation selected from Ca^{2+} or Mg^{2+} is meant, which are in a chemical sense not compounds but ions. Moreover, such cations, and Ca^{2+} and Mg^{2+} in particular, would appear to be the target analyte, to which the entire invention is aimed.

-Claim 5 is unclear since metal-dye complexes in general are formed by an initial charge transfer which

produces a dative bond between the dye molecule and the cation. Dative bonds, on the other hand, are known to be reversible. The degree of reversibility may change depending on the chemical nature of the complexes. Thus, an irreversible bond would appear to be contradictory.

-Claim 8 claims a method using the indicator of claim 1, which is bound to a product. Since the nature of the indicator and the product are unclear, claim 8 is unclear as well.

-The same applies with respect to claim 13.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Therefore, the independent claims are so broad, so unclear and so lack support by the description that a meaningful search on the basis of the claims as filed is impossible.

Consequently, the search was restricted to the following subject-matter:

- a composition for detecting Calcium or Magnesium (i.e. water hardness)
- comprising a metal indicator dye selected from the group or Alizarin Red, Eriochrome Black, Calmagite, or Murexide
- and the indicator dye being impregnated in a sheet of a fibrous material as derived from the description of the preferred embodiments.

Claim 8 and its dependent claims, were only searched insofar as they relate to this subject-matter. Claims 2, 4, 5, 9, 13-16 were not searched.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 02/01515

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5320969	A	14-06-1994	NONE	
US 5302531	A	12-04-1994	NONE	
JP 2082160	A	22-03-1990	JP 2696533 B2	14-01-1998
JP 51150392	A	23-12-1976	JP 925109 C	22-09-1978
			JP 52048839 B	13-12-1977

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☒ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.